

The effects of foaming conditions on plasticized polyvinyl chloride foam morphology by using liquid carbon dioxide

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Abstract. This research studies the effects of foaming conditions by using liquid carbon dioxide (CO₂) as a physical blowing agent on plasticized polyvinyl chloride (PVC) foam morphology. Foaming conditions were soaking time of 6, 10, and 12 h, foaming temperature of 70, 80, 90 °C for 5 s, at constant soaking temperature of -20 °C and pressure of 50 bar. Instantaneously increasing temperature was employed in this process for making foam structure. PVC foam samples were calculated percentage of shrinkage (Sh) by using density at before and after aging process at 30 °C for 12 h. When PVC samples were activated to form foam by using liquid CO₂ as a physical blowing agent, it reveal bimodal foam structure with a thick bubble wall (10-20 µm). Bubble diameter of PVC foam at longer soaking time is in the range of 40-60 µm and its at shorter soaking time reveal a large bubble that is in the range of 80-120 µm. Foaming condition slightly affected to bubble density that was in the narrow range of 10⁶-10⁸ bubbles/cm³. PVC foam reveal reduction of density up to 65% when compare with PVC and Sh is less than 10%.

1. Introduction

Polymer foam is defined as gas dispersed in polymer matrix such as polystyrene foam, polyethylene foam, polypropylene foam, polyvinyl chloride foam etc. Dispersed gas in polymer matrix can be generate into open-cell and close-cell structure [1]. The advantages of foam property are strength-to-weight ratio, low thermal conductivity, low electric constant, low density when compared with solid material. Thus, there are many applications of polymer foam such as auto motive parts, toys, electrical wire, food packaging, etc [2]. Each application require differential foam property, which relate to foam morphology and aging process after foam formation [3]. Therefore, there are three parameter to control foam morphology, polymer property, foaming process, and additive. Polymer properties are molecular weight, molecular weight distribution, melt flow index, polymer chain structure, amorphous polymer, semi-crystalline polymer, molecular orientation etc. When polymer property is optimized, foaming process is desired from polymer property such as, extrusion, injection mold, compression etc. Foaming process also consist of foaming conditions, temperature, time, pressure, flow rate, depressurization rate etc [4-7]. However, additive is chemical and/or physical material that is employed to adjust foam morphology such as, blowing agent, nucleating agent, plasticizer, fire retarding agent, etc. All of three parameters should be optimized to control foam morphology.

Basically of foaming process with using gas as physical blowing agent, there are four steps of foaming formation as shown in Figure 1 [8]. First, gas diffuse and dissolve in polymer matrix at desired conditions, time, pressure and temperature into heterogeneous/heterogeneous solution. Then, the system is activated by increasing temperature or decreasing pressure and nucleus generate during



nucleation step. After that, nucleus expand into a bubble or cell form during cell growth and then finally step is cell stabilization by air permeation into foam structure to replace gas.

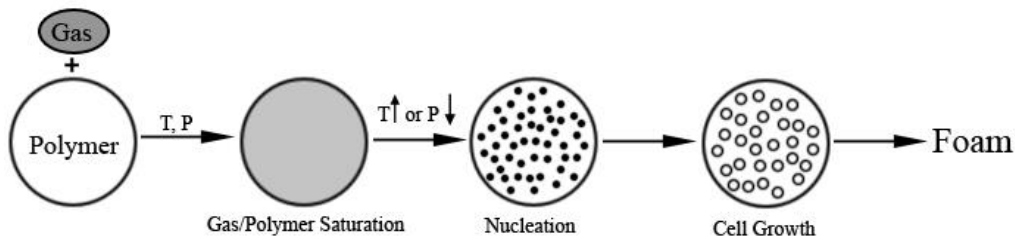


Figure 1. Foam formation for using gas as physical blowing agent.

This research selected amorphous polymer or plasticized polyvinyl chloride (PVC) to study PVC foam morphology because it is high margin of the construction industry in Thailand. PVC is foamed by using liquid carbon dioxide (CO₂) as blowing agent then it was left for aging process to observe shrinkage property.

2. Experiment and characterization

2.1 Foaming process

PVC sheet samples were soaked by using liquid CO₂ for 6, 10, and 12 h at constant temperature of -20 °C and pressure of 50 bar, as shown in Figure 2. After soaking step, these samples were immediately taken out and dipped in the silicone oil bath at desired foaming temperature (70, 80 and 90 °C) for 5 s to activate nucleation. PVC samples were cleaned and left for stabilization at 30 °C for 12 h then these samples were calculated the percentage of shrinkage (Sh) of the sample. The percentage of shrinkage is defined as the changing volume of PVC foam sample between before and after aging process and calculated by equation (1) which based on mass constant and neglect gaseous mass.

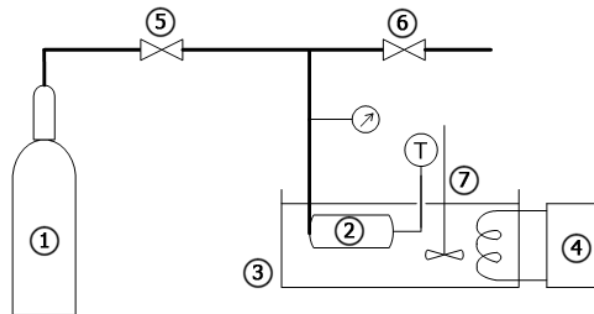


Figure 2. Schematic of soaking process by liquid CO₂ which including of CO₂ tank (1), 18 ml high pressure vessel (2), cooling bath (3), cooling unit (4), ball valves (5,6), and stirrer (7).

$$Sh = \left(\frac{V_{be} - V_{af}}{V_{be}} \right) \times 100 = \left(1 - \frac{\rho_{be}}{\rho_{af}} \right) \times 100 \quad (1)$$

when

V_{be}, V_{af} : before and after aging volume of PVC foam specimens, respectively (cm³)

ρ_{be}, ρ_{af} : before and after aging density of PVC foam specimens, respectively (g/cm³)

2.2 Foam morphology characterization

PVC foam samples were dipped in the liquid nitrogen (purchased from Linde (Thailand) Public Limited Company) for 30 s and cracked to observe PVC foam morphology at cross-sectional area.

These samples were coated by using the SC7620 sputter coater (Quorum Technologies Ltd.) and then were observed the foam morphology by using scanning electron microscope (MA10 from Carl Zeiss). SEM micrographs were characterized to obtain bubble diameter and bubble density (N), which calculate by equation (2) [9] as a function of number of bubbles (n) in observed cross-sectional area (A).

$$N = \left(\frac{n}{A}\right)^{3/2} \quad (2)$$

3. Results and discussion

PVC samples were soaked by liquid CO₂ at -20 °C, which below glass transition temperature of its, then it was activated foam by rapidly increasing temperature at desired foaming temperature. PVC density of before and after aging samples at various foaming conditions was presented in Figure 3, which can be represented the effect of solubility on foam density. Before aging PVC density at constant foaming temperature of 70 °C slightly decrease from 0.454 g/cm³ to 0.399 g/cm³ as soaking time but it strongly reduce from 0.695 g/cm³ to 0.556 g/cm³ at constant foaming temperature of 90 °C because liquid CO₂ molecules have more time to dissolve in PVC matrix and high nucleation rate at high temperature. After aging process, PVC foam density increased about 30%, it might be caused by rapidly diffusion rate of CO₂ escape from PVC structure that structure collapsed. Thus, PVC samples reveal percentage of shrinkage lower than 10%, as shown in Figure 4.

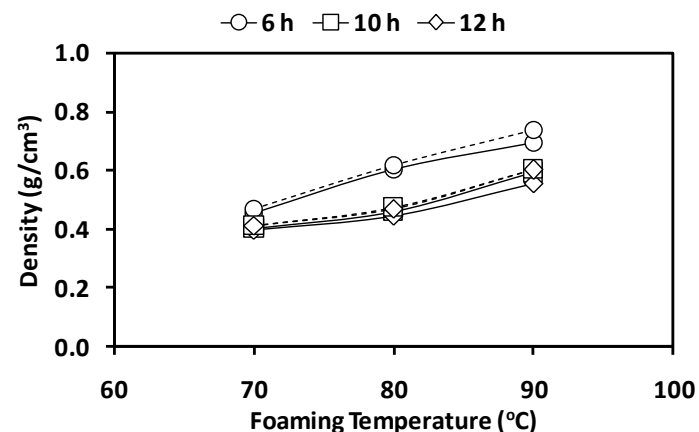


Figure 3. Before (solid line) and after (dashed line) aging density of PVC samples.

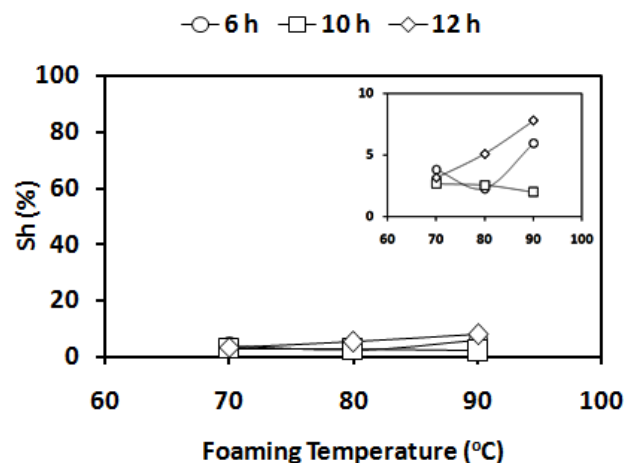


Figure 4. Percentage of shrinkage of PVC samples.

PVC samples morphology were observed by using SEM and shown in Figure 5. Effect of soaking time can be observed from top to bottom and effect of foaming temperature can be analyzed from left to right. PVC samples morphology have non-uniform and bimodal foam structure. At constant soaking time of 6 h, PVC samples morphology contain closed and slight open bubble structure with thick bubble wall. It might be caused by short time to dissolve of liquid CO₂ in PVC matrix that high melt strength restrict to bubble formation while nucleated bubble collapse and fuse with neighbour bubble. Thus, it is the highest foam density than other foaming conditions. Increasing foaming temperature affect to enhance nucleation rate that PVC samples can be observed more bubbles population with micro-scale. Improving nucleation rate can be involved by increasing solubility as soaking time of liquid CO₂ in PVC up to 10 and 12 h. PVC samples morphology reveal higher bubble population and bimodal foam structure, which approximately bubble size is larger than 50 μm and less than 10 μm . So, PVC samples with high solubility exhibit lower foam density than it at low solubility of liquid CO₂. Due to short foaming time during nucleation step, PVC matrix was not fully soft matrix, thus PVC samples display bimodal foam structure with thick bubble wall. That affect to high foam density and low shrinkage property.

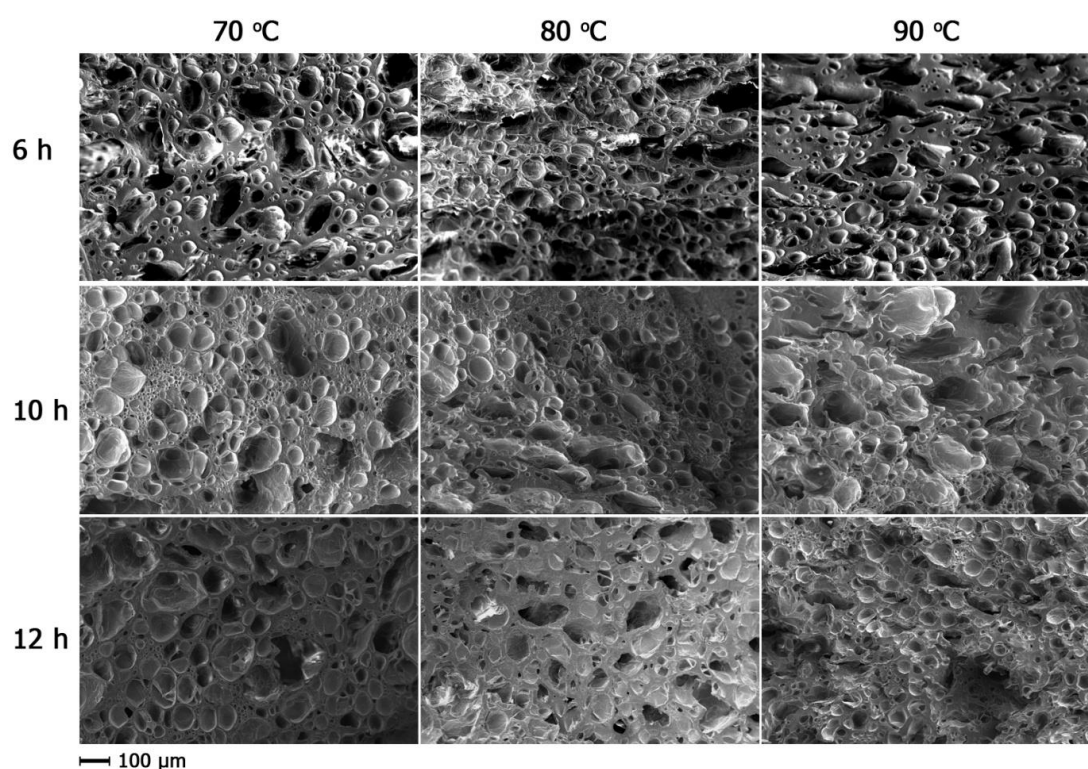


Figure 5. SEM micrographs of PVC samples as various foaming conditions.

As previous results, bubble diameter and bubble density of PVC samples were measured and plotted as a foaming condition, which shown in Figure 6 and Figure 7, respectively. PVC samples at constant soaking time of 6 h reveal 110 μm of bubble diameter at foaming temperature of 70 °C then bubble diameter drastically reduce to 75 μm and 70 μm as foaming temperature increased to 80 °C and 90 °C, respectively. It might be caused by enhancing nucleation rate and decreasing melt strength as increasing foaming temperature at low solubility of liquid CO₂ in PVC. However, critical radius is still a large size so nucleus collapse and fuse with neighbour nucleus to a large form or open bubble structure. When soaking time of CO₂/PVC system was increased up to 10 h and 12 h, more CO₂ diffused and dissolved into PVC matrix, which reduced melt strength PVC matrix. So that, nucleus formed and expanded into a bubble within the range of 40-60 μm . Moreover, increasing a foaming temperature from 70 °C to 90 °C at constant soaking time slightly affects to reduce bubble diameter.

To improve that foaming conditions enhance nucleation rate, bubble density was represented in Figure 7. Bubble density of PVC samples at constant soaking time of 6 h significantly increased from 3×10^6 to 2×10^7 bubbles/cm³ due to enhance nucleation rate by increasing foaming temperature. Liquid CO₂ in solid PVC matrix is slow diffusion, so that it favors to take a long time to achieve the saturated condition. Soaking time of CO₂/PVC system was extended to 10 h and 12 h, respectively, so that melt strength also reduced because of the plasticization effect of dissolved CO₂. Hence, PVC samples at soaking time of 10 h and 12 h reveal higher bubble density than PVC samples at soaking time of 6 h. On the other hand, increasing foaming temperature at soaking time of 10 h and 12 h slightly affect to the bubble density of PVC samples.

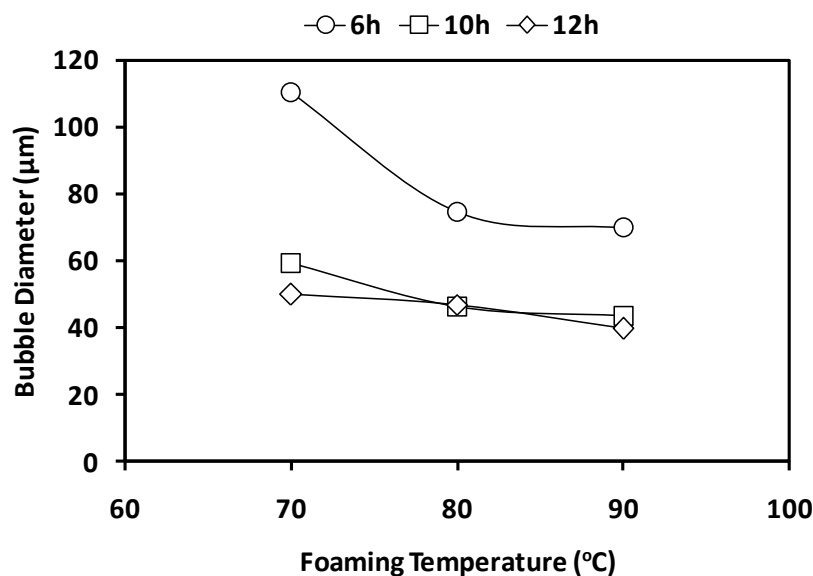


Figure 6. Effect of foaming temperature on bubble diameter of PVC samples.

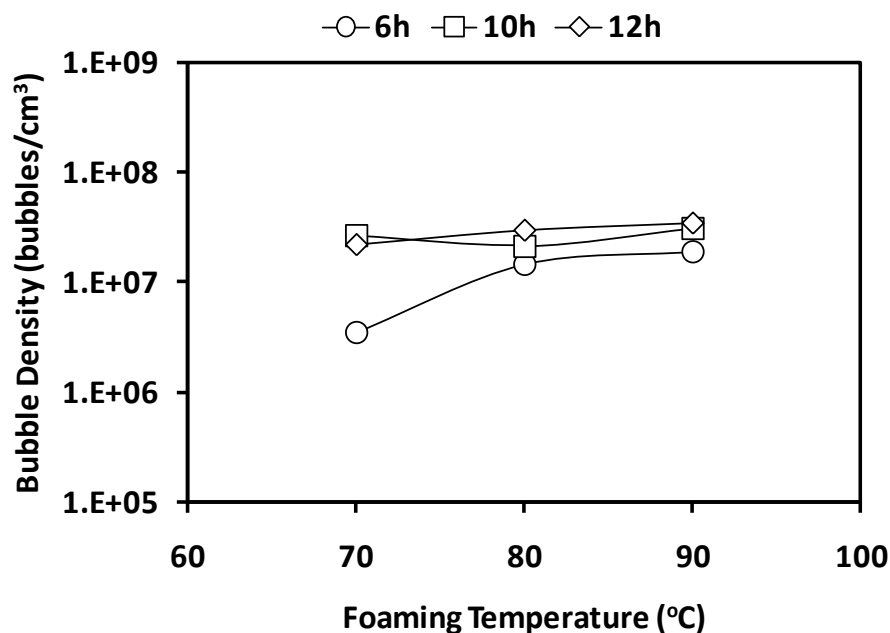


Figure 7. Effect of foaming temperature on bubble density of PVC samples.

4. Conclusion

Liquid CO₂ was employed as physical blowing agent during foaming process. PVC foam samples reveal bimodal foam structure with a thick bubble wall and partly exhibit slight open bubble structure. PVC foam samples density is in the range of 0.4 – 0.6 g/cm³ and after aging foam density slightly increased as before aging foam density. Thus, PVC foam samples demonstrate 10% of Sh.

5. References

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